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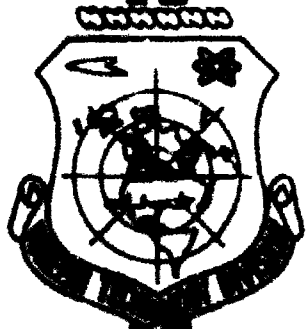
TRANSLATION

THE ROLE OF BACTERIA IN ELECTROCHEMICAL CORROSION OF STEEL IN SEA WATER

By

L. A. Rozenberg

FOREIGN TECHNOLOGY DIVISION



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THE ROLE OF BACTERIA IN ELECTROCHEMICAL CORROSION OF STEEL IN SEA WATER

BY: L. A. Rozenberg

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THE ROLE OF BACTERIA IN ELECTROCHEMICAL CORROSION OF STEEL IN SEA WATER

L. A. Rozenberg

Theoretically electrochemical corrosion of metals occurs during constant dipolarization of microgalvanic elements on the metal surfaces (Akimov, 1945; Rubenchik, 1950).

Metal is protected by very thin passive coatings from 10 to 150 A thick formed on the metal surface during its factory processing (Akimov, 1945; 1956). The protective properties of the passive surface coating characterize the electrode potential of the metal. The stronger it shifts to the positive side, the higher the protective properties of the passive layer and vice versa (Tomashov, 1952). A shift in electrode potential to the negative side is indicative that the passive surface layer has been destroyed to a certain extent. The sector with the highest negative electrode potential is the anode and that with the lowest negative potential is the cathode of the galvanic pair. The electrochemical processes lead to precipitation of molecular oxygen on the cathode and destruction of the anode, i.e., a corrosion process occurs. Further accumulation of oxygen molecules on the cathode polarizes it and halts further destruction

of the anode. In other words, cathode polarization is retarded and this stops corrosive erosion of the metal. For corrosion to proceed continuously, a constant depolarization of the cathode by binding oxygen molecules to some acceptor is necessary.

Thus, when metal is immersed in sea water the passive surface layer must first be destroyed. Then the microgalvanic pair arises and their work leads to corrosion.

Preceeding works conducted jointly with physical chemists I. B. Ulanovskiy and Yu. M. Korovin (Rozenberg, Ulanovskiy and Korovin, 1959; 1960; 1961) established that bacteria growing indirectly on the passive coating destroy its protective properties by shifting the electrode potential to the negative side and create favorable conditions for the earlier appearance of the microgalvanic pair.

Many authors have demonstrated the effect of bacterial products on iron and steel in water, particularly in sea water (Reynfel'd, 1939; Rubenchik, 1950; Nikitina and Ulanovskiy, 1954, 1957; Kuznetsov, 1959; Rozenberg, 1961; Kuznetsov and Verbitskaya, 1961; Updengraff, 1955; Abramo and Banfi, 1956; Payer and Payerova, 1956; Dauphin, 1956; Jamaguchi, Matuchasi and Aojama, 1957; and others). Most of the works studied the effect of sulfate-reducing bacteria on metal corrosion. Only in certain works are data given on biological corrosion caused by thiosulfate animonium-fixing, denitrifying and iron bacteria.

This work will study the role of sulfate-reducing and saprophytic bacteria in electrochemical corrosion of steel in sea water under laboratory conditions and determine the amount of corrosion damage to the metal. We separated a number of bacteria strains from the corrosion products of metal sheets immersed in the sea for a year.

Several types of bacteria were chosen from them for the tests.

METHODS

We put a culture of Desulfovibrio desulfuricans into 300 ml flasks with sea water under anaerobic conditions. Organic matter was poured into the water in the form of 0.35% sodium formate. The medium was autoclaved and immediately after cooling we inoculated the flasks with bacteria. We inoculated each flask with 8 ml of a 10-day-old culture on a Tauson medium. The tests were made on square sheets of 1X18H9T stainless steel with total working surfaces of about 15 cm^2. The specimens were suspended from polycaprolactam fibers. Several parallel flasks were simultaneously started and were taken in turn for analysis at the periods stated in the tables. The sterility of the control flasks was checked at the start and end of the test. When the sterility of the control was destroyed the test was scrapped and not counted. The saprophytic bacteria was cultured in the same manner but under aerobic conditions. We poured 0.05% peptone into the sea water instead of sodium formate. We inoculated the flasks with 0.5 ml of an aqueous mixture of a 2-day-old agar culture. All of the tests with saprophytic bacteria and part of those with Desulfofibrio desulfuricans were made on rectangular sheets of St-3 carbon steel with working surfaces of 10 cm^2. The control flasks and those inoculated with bacteria were placed in a thermostat at 25-27°. During analysis, we calculated the bacteria growing on the specimen surfaces. For this purpose we prepared scrapings from the whole overgrown area together with the products of corrosion; from the scrapings we prepared the necessary dilutions and inoculations. The adult colonies

of Desulfovibric desulfuricans were counted on a Tauson agar medium and the saprophyte cultures on beef extract agar.

We determined hydrogen sulfide by the iodometric method, and ammonia by colorimetry with Nessler's reagent by a FEK-M (photoelectrocolorimeter).

Weight loss of the specimen due to corrosion was determined by weighing them on analytical scales. Before weighing the specimens in flasks, they were carefully cleaned, polished, scoured with alcohol and sterilized by flame.

TABLE 1

The effect of Desulfovibrio desulfuricans on corrosion of 1X18H9T specimens

Test length, days	Control	With bacteria			Test length, days	Control	With bacteria		
	Weight loss, g/m²	Number of bacteria, 10³/cm²	H_2S mg/liter	Weight loss, g/m²		Weight loss, g/m²	Number of bacteria, 10³/cm²	H_2S mg/liter	Weight loss g/m²
5	—	6,7	15,4	—	30	0,008	44,2	38,5	0,048
10	—	10,7	15,1	—	154	—	24,1	38,1	—
15	—	17,4	15,1	—	435	0,080	4,7	31,2	0,135
20	—	32,4	23,6	—					

Note: a dash in all the tables means that a determination of that value was not made.

RESULTS

The Effect of Desulfovibrio desulfuricans on Corrosion of Stainless Steel

The data of Table 1 show that after 30 days the weight loss of the bacteria inoculated specimens was six times greater than that of the control. This indicates that the vital activity of Desulfovibrio desulfuricans causes biological corrosion. The value of biocorrosive damage to stainless steel increases when the metal is exposed to the culture for longer periods, although this creates

unfavorable conditions for bacterial growth.

The growth of Desulfovibrio desulfuricans cells on specimens of 1X18H9T steel and the formation of hydrogen sulfide in the medium stops after 150 days. We have shown earlier that Desulfovibrio desulfuricans reproduction and the accumulation of hydrogen sulfide in the medium ceases after 125 days of cultuvations (Rozenberg, 1961). L. I. Rubenchik (1950) noted that a arrest of growth of Desulfovibrio desulfuricans and the process of sulfate reduction in a medium, similar in composition to the Tauson medium, begins toward the end of the first month. From Table 1 it is also evident that after 150 days the number of bacteria decreased, and after 435 days their number is almost equal to the initial amount. The production of hydrogen sulfide has ceased altogether.

We met with two cases of exceptionally large weight loss in the bacteria inoculated specimens resulting from biological corrosion: (12.8 and 126.1 g/m^2). In both cases we observed local corrosive damage to the sides in the form of deep pits full of black graphitic corrosion products which were mainly FeS. There are no grounds to assume the presence of chemical corrosion by hydrogen sulfide, since the examined specimens were made from stainless steel, on which hydrogen sulfide is practically inactive. Unfortunately, we were unable to explain the cause of such severe damage to stainless steel. Nevertheless, these facts are interesting since they indicate that biological corrosion of stainless steel can be very intense when the culture is quite vigorous.

The following tests were conducted with St-3 carbon steel and lasted only 30-40 days. It was impossible to conduct longer tests because of the strong aggressiveness of sea water which causes

copious corrosion of the specimens even in the control flasks. The thick corrosion products formed on these specimens fell to the bottom of the flasks. The weight losses in the sterile specimens often reached 60-70 g/m² in 30-40 days.

The Effect of Desulfovibrio desulfuricans on Corrosion of Carbon Steel

In spite of all precautions, when the flasks were analyzed in turn a portion of the corrosion products was eroded by the medium and fell to the bottom of the flasks.

Therefore, the results of overgrowth analyses give lower quantities of bacteria. However, this partial loss of corrosion products does not affect the accuracy of determining specimen weight loss due to corrosion.

TABLE 2

The effect of Desulfovibrio desulfuricans on corrosion of St-3 steel specimens

Test length, days	Control			With bacteria				
	Weight loss, g/m²	Rate of corrosion g/m²/hr	Weight loss, %	Number of bacteria $10^3/cm^2$	H_2S mg/liter	Weight loss, g/m²	Rate of corrosion g/m²/hr	Weight loss, % of the control
10	9.2	0.03833	100.0	10.3	15.2	10.4	0.04333	113.0
20	—	—	—	28.8	21.7	20.8	—	—
30	—	—	—	33.8	20.1	31.3	—	—
40	40.7	0.04238	100.0	34.7	20.1	48.3	0.05052	119.2

Table 2 shows that on the test specimens the bacteria grew intensively throughout the test, energetically producing hydrogen sulfide. We observed biological corrosion of specimens already on the 10th day. Subsequently, biological corrosion increases, and after 40 days reaches 119.2% compared with the control.

The Effect of Saprophytic Bacteria on Carbon Steel Corrosion

Earlier it was established that the vital activity of Pseudomonas fluorescens and Bacillus mycoides shifts the electrode potential toward the negative side, which is an index of destruction of the passive surface layer of the steel (Ulanovskiy, Rozenberg and Korovin, 1960, 1961). We hypothesized that the potential also shifts due to the vital activity of other saprophytes.

TABLE 3

The effect of Pseudomonas fluorescens and Bacillus mycoides on corrosion of St-3 specimens

Test length, days	Control			With bacteria				
	Weight loss, g/m^2	Rate of corrosion $g/m^2/hr$	Weight loss, %	Number of bacteria $10^3/cm^2$	N/NH_4 mg/liter	Weight loss, g/m^2	Rate of corrosion $g/m^2/hr$	Weight loss, % of the control
Test with Ps. fluorescens								
5	10,6	0,08833	100,0	75,3	58,3	12,2	0,10166	115,1
10	—	—	—	300,0	75,2	19,8	—	—
15	—	—	—	420,6	79,4	44,9	—	—
30	29,6	0,04111	100,0	532,1	93,1	62,8	0,08722	212,1
Test with B. mycoides								
5	10,8	0,09000	100,0	20,0	55,2	13,4	0,11166	124,1
10	—	—	—	39,5	71,4	21,9	—	—
15	—	—	—	168,7	89,2	49,3	—	—
30	30,1	0,04180	100,0	215,8	101,3	63,2	0,08777	209,9

It is evident from Table 3 that Ps. fluorescens and B. mycoides grow well on St-3 specimens and energetically ammonificate the peptone. Bacillus mycoides forms colonies consisting of gelatinized threads which easily peel off of the specimens. When these gelatinized threads are shaken up with water in a test tube it is impossible to separate individual cells. Therefore, inoculation with such separations yielded a lower number of bacteria. Losses of corrosion products when the flasks were removed made calculation of these bacteria even more difficult. The production of ammonia

nicely characterizes the vital activity of both types of bacteria. It is a bit higher in B. mycoides. Here, biological corrosion is far more intensive than in the tests with Desulfovibrio desulfuricans. Even in the first 5 days the rate of corrosion for Ps. fluorescens was 115.1%, and for B. mycoides, 124.1%. For longer periods, corrosion increased and at the end of the test achieved for Ps. fluorescens 212.1% of the control, and for B. mycoides, 209.9%.

TABLE 4

The effect of saprophytic bacteria on corrosion of St-3 specimens

Culture	Test length, days	Control		With bacteria		
		Weight loss, g/m²	Rate of corrosion %	Number of bacteria, 10³/cm²	Weight loss, g/m²	Rate of corrosion, % of control
Bac. nitidus	15	11,2	100,0	416,7	21,3	190,1
	33	64,0	100,0	142,5	69,0	107,8
Bact. agile	15	11,2	100,0	1041,6	21,5	191,9
	33	60,0	100,0	402,0	61,0	101,7
Micrococ. albicans	15	11,2	100,0	210,1	31,3	279,4
	33	63,0	100,0	264,5	64,7	102,7
Micrococ. sphaeroides	15	20,3	100,0	303,0	40,4	199,0
	30	59,9	100,0	115,2	40,0	66,8
Sarcina citrina	15	19,9	100,0	363,8	31,1	156,3
	30	52,6	100,0	307,7	53,4	101,5
Bac. subtilis	16	30,9	100,0	1071,4	31,0	100,3
	38	61,5	100,0	1449,1	70,4	114,5

Table 4 introduces the corrosion losses of carbon steel in cultures of several types of saprophytic bacteria.

Saprophytic bacteria develop in sea water differently. Most of the types cause corrosive damage to steel. The bacteria vigorously reproduce on the surface of steel and energetically ammonificate. As is evident from Table 4, in 15-day-old cultures of all the bacteria except Bacillus subtilis, the corrosion rate of the inoculated specimens was 1.5-2.5 times higher than in the control. When the period was lengthened, further cell reproduction ceased, and we even noticed a drop in their quantity for a number of cultures.

When this happens, the biological corrosion rate also declines. Evidently, in longer periods the agressiveness of sea water arrests biological corrosion. Bacillus subtilis demonstrated its corrosive effect only at the end of the test. The remaining bacteria, Chromobacterium tremelloides, Bacillus lividus, Bacillus megatherium, and others not mentioned in Table 4, had even less effect on carbon-steel corrosion in sea water due to their weak vital activity under those conditions.

DISCUSSION OF THE RESULTS

By comp ring the obtained results with the data of earlier works and also with the data of other authors, we can schematically describe the process of bacterial corrosion of stainless and carbon steel in sea water.

Growing in anaerobic conditions on steel specimens in sea water supplied with organic substance and containing sulfates, sulfate-reducing bacteria play the role of depolarizers, activating the oxidation of hydrogen which accumulates on the cathode of the microgalvanic elements during electrochemical corrosion of steel. Carbon dioxide, accumulating in the medium due to gas exchange of saprophytic bacteria and as an end product of the oxidation of organic substance, destroys the protective properties of the passive surface layer of the steel. Its activation causes a sharp shift of electrode potential to the negative side and creates conditions for a more rapid development of the microgalvanic pair whose work enhances self-dissolution of steel. Bacteriogenic hydrogen sulfide and ammonia, being corrosive factors, produce corrosion in the form of ferrous sulfide and ferric hydroxide when they are in contact with

iron.

Not all the bacteria investigated caused biological corrosion of steel. We see the cause of this in the different rates of reproduction and vital activity of the bacteria. Only intensely reproducing forms with a well-expressed production of hydrogen sulfide and ammonia caused biological corrosion of steel.

Although our stainless steel weight losses due to biological corrosion over the course of a year were only about 0.002% of the metal mass, local biological corrosion of individual specimens reached 126 g/m^2, which is about 1.5% of the metal weight. We must pay particular attention to this phenomenon. Nevertheless, when separate areas of the steel sheet surfaces are being destroyed, especially powerful foci of corrosion can arise; due to this deep caverns are formed, causing severe damage to the metal. Bacterial corrosion of carbon steel, according to our tests, is always more severe. Calculations indicate that in tests with Desulfovibrio desulfuricans the carbon steel losses for a year can be about 1.6% of the metal mass, and with certain saprophytic bacteria, even 8-9%.

CONCLUSIONS

1. Bacteria play a role of biological depolarizers and activators in the process of electrochemical corrosion of steel in sea water.

2. The role of bacteria is very important in the initial period when they activate the metal surface and accelerate the formation of microgalvanic elements. Later on, corrosion of the metal becomes apparent due to increased use of molecular hydrogen and depolarization of the cathode, and due to the work of the galvanic pairs which

is maintained by the anode process and by the bacteriogenic hydrogen sulfide contacting the metal.

3. Only intensely reproducing bacteria with a well-expressed production of hydrogen sulfide or ammonia enhance the biological corrojion of carbon steel.

4. Most of the cultures studied cause biological corrosion of carbon steel leading to a significant loss of metal.

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